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(54) MANUFACTURE OF MAGNETIC THIN FILM

(57)Abstract:
PURPOSE: To provide a magnetic thin film having a low coercive force, high saturation magnetic flux density, and high permeability by a wet plating method having high mass-productivity.
CONSTITUTION: In this manufacturing method, a magnetic thin film is manufactured by heat-treating a Co-Fe alloy film formed by a plating method under a condition where the temperature rising rate is below 10° C/min and maximum temperature is below 350° C. Therefore, the magnetic thin film manufactured by this method can easily obtain high permeability.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The manufacture method of the magnetic thin film characterized by performing a vacuum 350 degrees C or less or heat-treatment under an inert atmosphere for the plating film which made Co and Fe the principal component in the programming rate of the following by 10-degree-C/.
[Claim 2] The manufacture method according to claim 1 characterized by performing the above-mentioned heat treatment all over a direct-current magnetic field or a rotation magnetic field.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to the manufacture method of the magnetic thin film formed by the wet galvanizing method. It is related with the manufacture method of the thin film especially used as magnetic pole material, such as the thin film magnetic head and a thin film transformer.
[0002]
[Description of the Prior Art] In addition to low coercive force, high saturation magnetic flux density, the low magnetostriction, etc., high permeability is demanded of the magnetic thin film of the thin film magnetic head or a thin film transformer.
[0003] Although it is common to be formed by the liquid phase forming-membranes methods, such as the gaseous-phase forming-membranes methods, such as a spatter, and electroplating, as for these magnetic thin films, membrane formation of a large area is easy for the liquid phase galvanizing method, and moreover a homogeneous high film is obtained, and there is an advantage that there are few man days in it.
[0004] Especially elevation of recording density in recent years has a large portion by elevation of the coercive force of a record medium. In order to fully write in a record medium with big coercive force, it is necessary to generate a stronger magnetic field from a recording head. For this reason, the high saturation-magnetic-flux-density material more than the nickel-Fe alloy (permalloy) currently widely used from the former is called for. A Co-Fe alloy is mentioned as a magnetic plating film which fills this magnetic-properties-demand (Japanese Patent Application No. 2-326813).
[0005] However, it was difficult to obtain high permeability from the former as compared with the nickel-Fe alloy which is used widely and which is hyposaturation flux density material comparatively.
[0006] Heat treatment after membrane formation is stress. For example, it is reported by the CoFeB amorphous film by the spatter that high permeability is obtained with heat treatment among [of 300 degrees C] a rotation magnetic field (collection [of the Institute of Electronics and Communication Engineers synthesis national conference drafts in the Showa 56 fiscal year] 1 -160).
[0007] Moreover, also in the galvanizing method, it is reported that heat treatment among a rotation magnetic field and a transverse magnetic field is effective (Japanese-Patent-Application-No. 3-122515 grade).
[0008] However, optimum conditions were determined only paying attention to heat treatment temperature and temperature fall speed. Especially as for temperature up temperature, attention was not paid in these cases. Although it was the inclination cut down since the temperature up with a rapid programming rate has generating of a crack etc., workability was considered, and a minute was used in comparatively high-speed about 15 degrees C /.
[0009]
[Problem(s) to be Solved by the Invention] the low coercive force which this invention was made from such a situation and formed by the galvanizing method -- high -- it is related with the

manufacture method which forms a saturation magnetic flux density thin film into high permeability
[0010]
[Means for Solving the Problem] this invention person came to find out that especially perform in detail condition examination in the case of heat treatment after the membrane formation known from the former, and high permeability is obtained, as a result of inquiring and inquiring wholeheartedly, in order to solve the above-mentioned technical problem.
[0011] Such a purpose is attained by this invention of following the (1) - (2).
[0012] (1) The manufacture method of the magnetic thin film characterized by performing heat-treatment of 350 degrees C or less under an inert atmosphere for the plating film which made Co and Fe the principal component in the programming rate of the following by 10-degree-C/.
[0013] (2) The manufacture method given in the above (1) characterized by performing the above-mentioned heat treatment all over a direct-current magnetic field or a rotation magnetic field.
[0014]
[Function] The magnetic thin film used for this invention is formed by the wet galvanizing method, i.e., electroplating, the electroless-plating method, the substitution galvanizing method, etc., and makes Co and Fe a principal component.
[0015] With such composition, the saturation magnetic flux density BS beyond 1.5T is obtained more than 1.2T, for example, especially as for the magnetic thin film of this invention, it is very useful as a magnetic thin film for the thin film magnetic head or thin film transformers.
[0016] However, permeability mu had many low things compared with the conventional NiFe alloy. 2000 or more (5MHz) permeability is easily obtained by the manufacture method of this invention.
[0017]
[Elements of the Invention] Hereafter, the concrete composition of this invention is explained in detail.
[0018] A programming rate is preferably taken as the following by 7.5-degree-C/the following by 10-degree-C/. Sufficient high permeability is not obtained as a programming rate is beyond the aforementioned range.
[0019] It is not reported at all until now that a programming rate is the important factor of permeability. Supposing this is a phenomenon peculiar to a plating film, it will be considered that the discharge and relation of hydrogen gas by which occlusion was carried out at the time of membrane formation are deep. However, it has not yet resulted in the elucidation.
[0020] A heat treatment maximum temperature makes less than 350 degrees C preferably 340 degrees C or less. The grain child growth whose heat treatment temperature is beyond the above-mentioned range becomes intense, and soft magnetic characteristics fall.
[0021] The holding time in a maximum temperature is good in 10 minutes - about 1 hour. Especially the total heating value that a sample receives in heat treatment of this invention is not a problem.
[0022] Not a factor also with an especially big temperature fall speed but natural air cooling is sufficient.
[0023] In order to prevent oxidization of a magnetic film as usually known, as for this processing, it is desirable to process under inert-atmosphere-izing or vacuum atmosphere. As an inert atmosphere, nitrogen, an argon, helium, etc. are common.
[0024] Moreover, although a magnetostriction changes with the iron / the cobalt ratios in a film, it is desirable to adjust bath composition so that it may become near zero mostly. Since a magnetostriction value changes with heat treatments, it will aim general at the magnetostriction value after heat treatment.
[0025] By membrane formation by the electroless-plating method, B or P contains 0.1 to 10% of the weight on a film by the eutectoid from a reducing agent. When especially an amine borane system is used as a reducing agent, soft-magnetism-izing is easy and is considered because the effect is large by particle detailed-ization. The eutectoid of P and B is possible by adding B and P compound to a bath also in electroplating.

[0026] In addition, improvement in a RF property and anti-corrosion disposition superiors are also further expected to the magnetic alloy of this invention by containing one or more sorts of elements chosen from C, S, Cr, Cu, Sn, Ru, Au, Pd, Ag, Mn, In, Mo, Pb, Re, W, Zn, Zr, Rh, Pt, etc. 3 or less % of the weight. Moreover, these elements are used as an impurity, and since especially trouble is not accepted, the cost reduction by use of a cheap reagent is also possible also for carrying out minute amount content.
[0027] However, in 3% of the weight or more of content, since it has a bad influence on magnetic properties or the fall of Bs is caused in many cases, cautions are required.
[0028] Moreover, in order to control a magnetic anisotropy positively, processing among a magnetic field is effective. Heat treatment among a transverse magnetic field to which the time of the inside of a rotation magnetic field or membrane formation and a transverse magnetic field are applied as processing of a soft-magnetism thin film is known [both], and it is effective.
[0029] The magnetic thin film of this invention has the outstanding permeability. Specifically, this is [at 5MHz] equivalent to a permalloy at 2000 or more.
[0030] Especially the plating film preferably used by this invention is formed by the electroless-plating method or electroplating.
[0031] In a plating bath, cobalt ion and iron ion are contained at least. It is desirable to use water-soluble salts, such as a sulfate, a chlorination salt, a sulfamate, acetate, and a nitrate, as the cobalt ion used by this invention and an iron ion source of supply. Or the ion which was made to dip a metal during a plating bath and carried out the natural dissolution, and the ion which dissolved by electrolysis as an anode plate can also be used effectively.
[0032] As for especially the concentration of cobalt ion, it is desirable that 0.05-5 mols /are [l.] 0.1-2 mols/l. If the fall of deposit speed is remarkable in the concentration of cobalt ion being under the aforementioned range and the aforementioned range is exceeded, the viscosity of a plating bath will rise and, generally membrane formation into workability or a detailed resist pattern will become difficult.
[0033] Moreover, the iron ion concentration under plating bath is 0.01-1 mol/l. more preferably in the range of 0.001-1 mol/l. What is necessary is just to determine that desired film composition is acquired, since it is the big factor which determines composition of the film with which the ratio of concentration with cobalt ion is formed.
[0034] As iron ion, divalent iron ion is desirable. However, divalent iron ion oxidizes and tends to turn into trivalent iron ion. If trivalent iron ion is a small amount, there may be an effect in the leveling nature instead of a problem etc. Moreover, returning to divalent iron ion easily is possible, and it is also easy to prevent generation.
[0035] Generally using the side reaction at the time of dipping the metal of the addition and Co of a reducing agent like an ascorbic acid, hypophosphorous acid, dimethylamine borane, thiourea or those salts, and a derivative as the reduction method, and Fe in a plating bath, and carrying out the natural dissolution is known.
[0036] Moreover, as for especially pH of a bath, in the case of electroplating, 2.0-3.0 are desirable at 1.0-4.0. Membrane formation speed is slow in below the above-mentioned range, and it is easy to produce sedimentation of trivalent iron above the aforementioned range. As for surfactants, such as electric conduction salts, such as buffers for pH, such as a way acid besides these, an ammonium sulfate, and an ammonium chloride, and a sodium lauryl sulfate, etc., during a plating bath, it is desirable that the component added by the usual electroplating bath contains.
[0037] In the case of an electroless-plating method, a reducing agent is added. As a reducing agent, hypophosphorous acid, its salt, dimethylamine borane (DMAB), the trimethylamine borane, the hydrazine, etc. are known widely. Especially DMAB is desirable. As for pH of a bath, in the case of a DMAB bath, about nine are desirable.
[0038] Moreover, in order to obtain especially soft magnetic characteristics, it is desirable to contain the ammonium ion, especially the ammonium chloride during a plating bath. However, the cause is unknown.
[0039] In order to give a uniaxial anisotropy in the direction of the purpose, it is desirable among a direct-current magnetic field and a transverse magnetic field to perform membrane formation

among a rotation magnetic field. In membrane formation among a rotation magnetic field, an anisotropy is given among a transverse magnetic field by holding whether a strong magnetic field is impressed every 90 degrees for a long time etc.
[0040] Moreover, a plating bath needs to remove the particle and hydroxide under bath by continuation filtering to obtain outstanding magnetic properties. When capacity of a plating bath is made into V l. as a grade of filtration, the above is desirable by Vx0.1l./as a filtration flow rate. Although a filter mesh is based on a use, in membrane formation into an especially detailed resist pattern, its 0.2 micrometers or less are desirable.
[0041] TiPt of non-solubility [viewpoint / of particle removal] and the ferrite electrode of an anode plate are desirable. However, since oxidation reaction occurs in an anode plate, it is desirable to dissociate with the cathode section by ion exchange membrane.
[0042] As a solvent of the plating bath of this invention, a non-drainage system solvent, for example, methyl alcohol, ethyl alcohol, propylene carbide, fused salt, etc. are [other than usual water] usable.
[0043]
[Example] Hereafter, the concrete example of this invention is shown and this invention is further explained to a detail.
[0044] 50A and the substrate which did 500A membrane formation of copper further were used for titanium by the spatter on the glass of the part number 7059 by example 1 Corning, Inc. After dipping in 1N-hydrochloric acid (ordinary temperature) for 30 seconds as plating pretreatment and rinsing, the electroless-plating sample which shows a magnetic film in the following table 1 using the following plating bath on the following plating conditions was produced.
[0045] Electroless-plating bath composition (inside of 1l.)
cobalt sulfate 0.1-mol iron sulfate (II) 0.0025-mol ammonium sulfate 0.30-mol dimethylamine borane 0.025-mol tartaric acid 0.60-mol plating bath temperature -- pH of 70 degrees C and a plating bath -- 9.0 -- it came out, and plating time was set as for about 10 minutes, and impressed the direct-current magnetic field of 600 Oe
[0046] Thickness of a sample was set to 1 micrometer. When composition of a sample was analyzed using X-ray fluorescence equipment and ICP, it was B=3.9at% Fe=5.1at% Co=91at%. Saturation magnetic flux density Bs was 1520 emu(s)/cc and coercive force Hc=0.5Oe.
[0047] Permeability measurement was performed after heat treatment on the conditions shown in Table 1 to each sample. A result is shown in Table 1. Heat treatment is among the transverse magnetic field which gives a magnetic field to the field inboard which intersects perpendicularly with the time of membrane formation in nitrogen-gas-atmosphere mind. The temperature fall considered the holding time in a maximum temperature as natural air cooling for 20 minutes.
[0048]
[Table 1]

サンプル番号	昇温速度 (℃/分)	最高温度 (℃)	最高温度での保持時間 (分間)	磁場強度 (Oe)	透磁率 5MHz (-)
1 (比較)	15	150	30	2000	1300
2 (比較)	10	150	30	2000	1300
3	7.5	150	30	2000	2100
4	3	150	30	2000	2600
5	3	150	10	2000	2000
6 (比較)	10	200	30	500	1400
7 (比較)	10	200	30	1000	1300
6	5	200	30	500	2600

[0049] (Saturation magnetic flux density Bs) It measured by VSM.
[0050] (Permeability) It measured by 5MHz and 3mOe magnetic field using the character coil

type permeameter of 8.
[0051] (Coercive force Hc) It measured with 60 Hz-BH marker.
[0052] 50A and the substrate which did 500A membrane formation of a permalloy further were used for titanium by the spatter on the glass of the part number 7059 by example 2 Corning, Inc. The magnetic film was formed on the following electroplating conditions after the processing of conditions same as plating pretreatment as an example 1.
[0053] Electroplating-bath composition (inside of 1l.)
Sulfamine cobalt 0.2-mol sulfamine iron (II) 0.01-mol ammonium chloride 10g way acid It is 1, 3, and 6-naphthalene tris RUHON acid TORINA thorium 40g. 60g propargyl alcohol pH of 40 degrees C and a plating bath set 1 A/dm2 and plating time to 2.8, and 0.05ml plating bath temperature set current density as for 5 minutes, and it performed electroplating, impressing the direct-current magnetic field of 600Oe.
[0054] Thickness of a sample was set to 1 micrometer. When composition of a sample was analyzed using X-ray fluorescence equipment and ICP, it was Fe=4wt% Co=96wt%. Saturation magnetic flux density Bs was 1.6T and coercive force Hc=0.5Oe.
[0055] Permeability measurement was performed after heat treatment on the conditions shown in Table 2 to each sample. A result is shown in Table 2. Heat treatment is among the rotation magnetic field of 60rpn(s) in a vacuum. The temperature fall considered the maximum-temperature holding time as natural air cooling for 30 minutes.
[0056]
[Table 2]

サンプル番号	昇温速度 (℃/分)	最高温度 (℃)	最高温度での保持時間 (分間)	磁場強度 (Oe)	透磁率 5MHz (-)
8 (比較)	15	330	60	1000	1500
9 (比較)	10	330	60	1000	1500
10	5	330	60	1000	2600
11	3	330	60	1000	3000
12	1	330	10	1000	2700

[0057] From the result of the above example to a book That is, according to this invention, a high permeability magnetic thin film is obtained easily.
[0058]
[Effect of the Invention] According to this invention, a high permeability magnetic thin film is obtained easily. And productivity high for the galvanizing method is acquired.

[Translation done.]